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**OXIDATION-RESISTANT METALLOCENES. THE SYNTHESIS
AND PROPERTIES OF PERCHLOROFERROCENE
AND RELATED POLYCHLORINATED AND
FLUORINATED FERROCENES**

FREDERICK L. HEDBERG

HAROLD ROSENBERG

TECHNICAL REPORT AFML-TR-69-270

APRIL 1970

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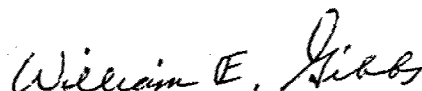
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FOREWORD

This report was prepared by the Polymer Branch of the Nonmetallic Materials Division, Air Force Materials Laboratory. The work was conducted under Project No. 7342, "Fundamental Research on Macromolecular Materials", Task No. 734201, "Basic Factors in the Synthesis of Macromolecular Materials". It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. Harold Rosenberg as Project Scientist.

This report covers research conducted from May 1968 to May 1969.

This technical report has been reviewed and is approved.

A handwritten signature in cursive script that reads "William E. Gibbs".

WILLIAM E. GIBBS
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

Two complete series of novel polychlorinated derivatives of ferrocene, $(C_5H_{5-n}Cl_n)_2Fe$ and $C_5H_{5-n}Cl_nFeC_5H_5$, were prepared and fully characterized. In one series, compounds in which both rings of the metallocene contain the same number (from two to five) of chlorine atoms were synthesized. Included in this group is decachloroferrocene, the first metallocene derivative completely substituted with electron-withdrawing atoms. The more highly chlorinated members of this series exhibited both a degree of oxidative stability heretofore unobserved in any metallocene and an unpredicted high thermal stability.

The second series of polychlorinated ferrocenes was composed of compounds in which one ring of the metallocene was substituted with from two to five chlorine atoms while the other ring was unsubstituted. This series of derivatives exhibited a decrease in thermal stability with increased chlorine content, indicating that symmetry effects were probably instrumental in providing thermal stability to the first series.

As a first step toward the synthesis of fluorine analogs of the polychlorinated ferrocenes, the preparation of fluoroferrocene was accomplished. This compound represents the first known organometallic derivative in which a fluorine atom is directly bonded to a metallocene ring.

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Introduction

One of the chemical systems which has been of considerable interest to the U. S. Air Force as a source of nonmetallic materials with high thermal and radiation resistance is the metallocene family of organometallic compounds. Metallocene-containing polymers have potential for a number of aerospace materials applications, such as ablative plastics for heat shields and structural laminates for low weight radiation shields, while liquid metallocene derivatives may be useful both as high-temperature lubricants or additives and as high density fluids.

The major barrier to the further development and actual utilization of metallocene-type materials in such applications has been the ease of oxidation of these compounds which has restricted their use in the presence of air or other chemical oxidants. It has long been known that the oxidation resistance of metallocenes can be increased by the incorporation of electron-withdrawing substituents into the five-carbon rings, but, until now, no method has been found to fully substitute the rings with such atoms or groups. Furthermore, it has been the belief of a number of chemists working in the area that metallocenes substituted in this manner would completely lose their thermal stability.

This report describes the preparation of two series of polychlorinated ferrocene derivatives, including decachloroferrocenes (or perchloroferrocene), the first metallocene compound completely substituted with electron-withdrawing substituents. The unique oxidation resistance as well as the

thermal stability, of this and the other highly chlorinated ferrocene compounds is described.

Polyfluorinated ferrocenes should display even higher oxidation-resistance than their polychlorinated analogs due to the greater electron withdrawing power of the fluorine atom. The unique physical and chemical stabilities associated with polyfluorinated materials of both the aliphatic and aromatic types provide further impetus for the synthesis of polyfluorinated ferrocenes. No derivative of ferrocene has yet been reported in which a fluorine atom is directly bonded to the ferrocene ring. This report describes the initial synthesis of the first such compound, fluoroferrocene.

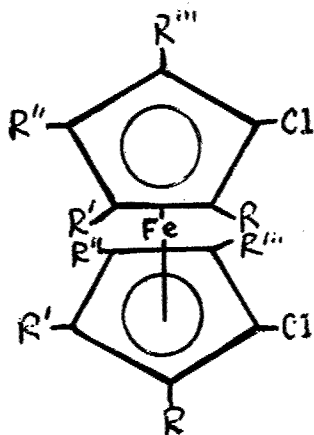
DISCUSSION AND EXPERIMENTAL

Although the thermal stability of ferrocene and ferrocene polymers is well known, the utilization of ferrocene derivatives for high-temperature materials has been restricted by the characteristic instability of the ferrocene system toward chemical oxidation as well as air oxidation at elevated temperatures. The resistance of ferrocene toward chemical oxidation can be enhanced by the incorporation of electron-withdrawing substituents on the ferrocene ring. It has been shown that the effect of two such substituents on the oxidation potential of ferrocenes is roughly additive whether the substituents are located heteroannularly (Reference 1) or homoannularly (Reference 2). Although this additive effect might be expected to diminish with additional electron-withdrawing substituents, substantial enhancement of oxidation resistance should result from complete substitution of the ferrocene rings by electron-withdrawing substituents. The only reported decasubstituted ferrocene derivatives, 1,1',2,2',3,3',4,4',5,5'-decamethylferrocene (References 3 and 4) and -decaethylferrocene (Reference 5), contain solely electron-donating alkyl groups. The formation and high melting points of these compounds indicate, however, that there is no overwhelming steric barrier to decasubstitution in general.

A second barrier to decasubstitution which must be considered for electron-withdrawing substituents is their possible deleterious effect upon the metal-to-ring bonding. Some authors (Reference 3) have stated

that π -cyclopentadienyl derivatives which are completely substituted with electronegative substituents would not likely be stable.

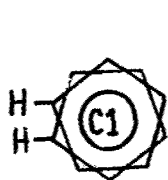
In order to ascertain whether or not such compounds would possess both oxidative and thermal stability, the attention of the present workers has been centered upon the synthesis of perhalo, and specifically, deca-chloro and decafluoro derivatives of ferrocene and ruthenocene. In this report, the preparation and properties of the first perhaloferrocene, 1,1',2,2',3,3',4,4',5,5'-decachloroferrocene, a metallocene derivative displaying both thermal stability and unique oxidative stability, are described. In addition, the synthesis of two series of polychlorinated ferrocenes, I b-e and III b-e, was carried out as part of the general investigation of polyhalo metallocene derivatives. The preparative routes to and significant characteristics of these unique compounds are discussed only briefly in this initial report on polyhalogenated metallocenes.



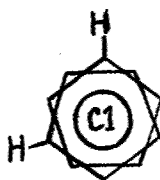
- Ia. R, R', R'' and $R''' = H$
- Ib. $R=Cl$; R', R'' and $R''' = H$
- Ic. R and $R' = Cl$; R'' and $R''' = H$
- Id. R, R' and $R'' = Cl$; $R''' = H$
- Ie. R, R', R'' and $R''' = Cl$
- If. $R=Li$; R', R'' and $R''' = H$
- Ig. R, R' and $R'' = Cl$; $R''' = Li$

The preparation of decachloroferrocene (Ie) was initiated by the reaction of 1,1'-dichloroferrocene (Ia) with n-butyllithium to give 1,1'-dichloro-2,2'-dilithioferrocene (If), followed by exchange chlorination of If with hexachloroethane according to the method of Hauser and coworkers (Reference 6) to give 1,1',2,2'-tetrachloroferrocene (Ib). By a similar procedure, Ib was converted to 1,1',2,2',3,3'-hexachloroferrocene (Ic), Ic was converted to 1,1',2,2',3,3',4,4'-octachloroferrocene (Id) and Id was converted to Ie. Anal. Calcd for $C_{10}Cl_{10}Fe$: C, 22.64; Cl, 66.83; Fe, 10.53. Found: C, 22.85, 22.82; Cl, 66.31, 66.32; Fe, 9.75, 9.72. Mass spectroscopy afforded a parent peak group with the required isotopic masses and distribution. The infrared spectrum (Figure 1) of Ie in the region from $4000-250\text{ cm}^{-1}$ showed only seven bands, at 1350, 1307, 702, 509, 412, 378, and 368 cm^{-1} . No nmr signals were obtained.

Compounds Ib, Ic, and Id were fully characterized by elemental analyses as well as infrared nuclear magnetic resonance, and mass spectroscopy. The following melting points and corresponding decomposition temperatures for the polychlorinated compounds indicate an increase in thermal stability with increasing chlorine content: Ib, mp $141-142^{\circ}$, dec $190-210^{\circ}$; Ic, mp $179-181^{\circ}$, dec $190-210^{\circ}$; Id, mp $162-172^{\circ}$, dec $225-230^{\circ}$; Ie, mp 245° (dec). The same decomposition point was obtained for Ie when a sample was heated in either air or under nitrogen. The broad range obtained for the mp of Id may be attributed to the presence of a substantial energy barrier between the rotational isomers IIa, IIb and IIc.



IIa



IIb

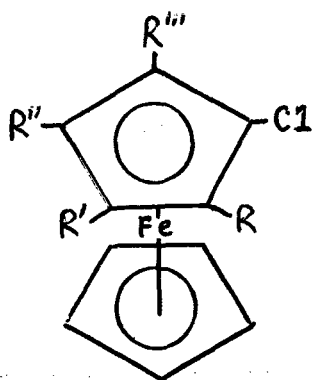


IIc

The anticipated stability of the higher polychlorinated ferrocenes toward chemical oxidation was substantiated by treatment with strong oxidants. Both Id and Ie were totally unaffected by either concentrated nitric acid or concentrated sulfuric acid at 100°. No metallocene compound showing similar stability toward nitric acid has been reported to date. A solution of bromine in carbon tetrachloride showed no change in color upon addition of Ic, Id or Ie.

The potential utility of Ie for the synthesis of other perchloroferrocene derivatives was demonstrated by reacting Ie with *n*-butyllithium at temperatures below -40° to form the dilithiated intermediate (Ig), which upon hydrolysis afforded Id in quantitative yield.

The effect of symmetry in stabilizing compounds of the type exemplified by Ie can be seen by contrasting the increase in thermal stability with increasing chlorine content, as exhibited by compounds Ib-Ie with the opposite trend shown in the series of compounds IIIb-IIIe. The latter



IIIa. R, R', R'' and $R''' = H$

IIIb. $R=Cl$; R', R'' and $R''' = H$

IIIc. R, R' and Cl ; R''' and $R'' = H$

IIId. R, R' and $R'' = Cl$; $R''' = H$

IIIe. R, R', R'' and $R''' = Cl$

derivatives were synthesized by a stepwise procedure analogous to that used for compounds Ib-Ie, with chloroferrocene (IIIa) as the starting material. One member of this series, IIIb, was reported previously by Russian workers who prepared it by an alternate procedure (Reference 7). The structures of compounds IIIb-IIIe were completely confirmed by elemental, together with infrared, nuclear magnetic resonance and mass spectral, analysis. The melting points and decomposition temperatures found for this series of compounds were as follows: IIIb, mp $88-90^{\circ}$, dec $210-220^{\circ}$; IIIc, mp $103.5-104.5^{\circ}$, dec $200-210^{\circ}$; IIId, mp $81-82^{\circ}$, dec $180-190^{\circ}$; IIIe, mp $143-144^{\circ}$, dec 150° .

Full experimental details of the syntheses of all compounds, together with results of NMR, mass spectral, crystallographic and polarographic studies now in progress, will be presented in forthcoming technical reports.

The reaction of organolithium compounds with perchloryl fluoride to give the corresponding organofluorine compounds has been recently reported (Reference 8). The preparation of pure ferrocenyllithium in high yield

from bromoferrocene and n-butyllithium has been developed in this laboratory (Reference 9). Addition of perchloryl fluoride at -70° to a solution of ferrocenyllithium in ether-THF, followed by reduction of the reaction mixture by aqueous sodium thiosulfate and purification by column chromatography, afforded a 10% yield of fluoroferrocene, mp, $116-118^{\circ}$. The structure of the compound has been confirmed by infrared, nuclear magnetic resonance and mass spectral analysis.

Work is presently underway to synthesize 1,1'-difluoroferrocene by an analogous reaction, using perchloryl fluoride and 1,1'-dilithioferrocene. It is anticipated that lithiation of these fluorinated ferrocene derivatives will take place in the 2 and 2' positions and that subsequent reactions with perchloryl fluoride will lead to a series of polyfluorinated ferrocenes analogous to the previously described polychlorinated ferrocenes.

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FLUOROFERROCENE						
SYNTHESIS						
ORGANOMETALLIC						
ELECTRON-WITHDRAWING SUBSTITUENTS						

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